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SURFACE CONTAMINATION OF ADHESIVE BONDING MATERIALS

W. L. BAUN

J. S. SOLOMON

*MECHANICS AND SURFACE INTERACTIONS BRANCH
NONMETALLIC MATERIALS DIVISION*

DECEMBER 1979

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Final Report for Period January 1978 — September 1979

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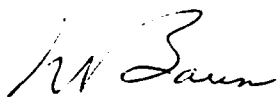
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This technical report has been reviewed and is approved for publication.


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ion mass spectroscopy were used to characterize adhesive bonding materials as received and at various prebonding stages. The presence of contaminants or undesirable materials has been traced to manufacturing processes, prebonding treatments, and environment. In many instances the presence of contaminants or unwanted materials has been directly related to poor bond performance.

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FOREWORD

This technical report was prepared by W. L. Baun of the Mechanics and Surface Interactions Branch, Nonmetallic Materials Division, Air Force Materials Laboratory and J. S. Solomon, University of Dayton Research Institute. The work was initiated under Project 2419, "Nonmetallic and Composite Materials" and WUD #44, "Improved Materials, Processes and Life Prediction Methodology of Adhesive Bonding", monitored by Dr. T. W. Haas. A portion of the work was carried out in a program of cooperative research under AF33615-76-C-5185.

This report covers work conducted inhouse and contractually during the period January 1978 - September 1979. The results herein were partially presented at a symposium on contamination held in Washington, D.C., September 1978.

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SECTION I

INTRODUCTION

The presence of unwanted chemical species within the interphase^{1,2} region of an adhesive bond becomes an extremely important consideration in the overall performance of bonded materials. This region includes all the material from some point in the bulk adhesive toward and through the boundary between adhesive and adherend to a point in the adherend where the local properties are the same as the bulk properties. Contaminants or unwanted materials within this region, originating from the original adherend surfaces, adherend bulk, and bulk adhesive, can adversely affect bonding mechanisms (i.e., wetting and adhesion) as well as bond performance (i.e., strength and durability)³. This becomes a very crucial problem when applying adhesive bonding to aircraft primary structure fabrication. Table I lists the principle points at which contaminants or unwanted chemical species can be introduced into the component materials of adhesively bonded structures.

Initially, many impurities are introduced in the raw materials long before the actual use in adhesive bonding during manufacturing and processing steps. The next possible entry point for contaminants can occur after the materials are received and prepared for bonding. Prebonding treatments generally are designed to mechanically or chemically alter the original adherend surfaces. The various chemical solutions (i.e., acid etches and degreasing solvents) used in these steps certainly are potential sources for contamination of the adherend surface. The problem is further complicated when alloys are chemically treated since the alloy constituents may be subject to segregation, selective chemical attack, or smutting. Finally, the environment and handling before and

TABLE I. SOURCES OF CONTAMINANTS OR SPECIES WHICH
COULD AFFECT ADHESIVE BONDING AND BOND
PROPERTIES

1. Raw Materials Processing
 - a. Adherend
 - b. Adhesive
2. Prebonding Treatments
 - a. Chemical solution contributions
 - b. Alloy constituents
3. Environment
 - a. Storage and handling
 - b. Bonding

during the actual bonding can introduce contaminants or even physically alter the adherend surfaces.

The problem in trying to establish some acceptable level of impurities in bonding materials is twofold: first, the processing steps are usually proprietary and therefore their exact chemical content is not specified; and second, a chemical analysis may not be useful since impurities such as highly mobile sodium may diffuse to the surface during cure cycles resulting in localized high concentrations. Contamination problems may be minimized by the proper choice and control of materials and effective bonding pretreatments. However, the only guarantee that the proper choices are being made is the establishment of a thorough surface characterization program. In our investigations of adhesive bonding phenomena, surface analysis methods, such as Ion Scattering Spectrometry (ISS), Secondary Ion Mass Spectrometry (SIMS), and Auger Electron Spectrometry (AES) were used to chemically characterize the surface of materials which make up adhesively bonded structures. Not only are these techniques necessary for prebonding studies, but contribute immensely to the overall performance and long term durability studies of bond joints by providing chemical information from failed surfaces.

In this report examples of surface characterization data from ISS, SIMS, and AES are presented which identify the chemical species introduced to the bonding materials at the various stages outlined in Table I. In some cases a correlation is made with surface contamination and bond performance.

SECTION II

SOURCES OF CONTAMINATION

1.0 RAW MATERIAL

a. Adherend

The basic adherend materials used for adhesively bonded structures in aircraft applications are 2024 Al, 7075 Al, 6Al-4V-Ti, and graphite fiber composites. The adhesives are thermosetting epoxies with a Nylon or Dacron mat carrier. Aluminum and titanium undergo many steps in their processing before finally being rolled into sheets of either the pure metal or various alloys. Table II lists some of the prominent impurities that either exist naturally in the original ore or which are introduced during processing, heat forming and fabrication, and heat treatment. In several areas of processing such as the use of a flux in skimming of the molten bath, it appears that little thought is placed to the possible consequences to adhesive bonding by adding such materials as sodium, potassium, and chlorine into the melt.

Four aluminum alloys studied were 2024, 7075, 7050, and 6061. Their nominal compositions are listed in Table III. Auger spectra in Figures 1 and 2 show the surface compositions of the "as received" alloys to be totally different from the bulk compositions listed in Table III. In fact the surfaces appear to be a magnesium rich oxide which is probably the result of the heat treatment step during final processing. The in-depth elemental profiles, represented in Figure 2 by the Auger dN/dE signal strength as a function of ion sputtering time, show that this oxide layer on 6061 aluminum to be approximately 1000A in thickness and the magnesium content decreases with oxide thickness. Similar results were found with "as received" sheets of the other three alloys⁴.

TABLE II. INTRODUCTION OF IMPURITIES IN OR ON ALUMINUM

<u>Process</u>	<u>Common Impurity</u>	<u>Mechanism</u>
Melting	Si ore Fe impurity	Al + SiO ₂ Al + Fe ₂ O ₃
Skimming	Na, K, Cl	Flux
Degassing	Cl, Mg, Zn	Flux
Remove Inclusions	Na, Cl, K	Flux
Forming	C	Lubrication
Fabrication	C, S, Cl (soaps, oils, greases)	Lubrication
<u>Heat Treating</u> (Solution heat treatment, 950- 1000°F)	KNO ₃ , KNO ₃ /NaNO ₃ K ₂ Cr ₂ O ₇ Silica Sand	Salt Bath Salt Bath Corrosion Inhibitor Fluidized Beds
Precip. heat treats 300°F-500°F	H ₂ O, O, N, CO ₂ , CO, SO ₂ , SO ₃ , NH ₃ , H ₂ Mg and others (Diffusion of Alloying Elements through Al clad)	Furnace Atmosphere Excessive Temp

TABLE III. NOMINAL CHEMICAL COMPOSITION OF ALUMINUM ALLOYS³

<u>Alloy</u>	<u>Si</u>	<u>Cu</u>	<u>Mn</u>	<u>Mg</u>	<u>Cr</u>	<u>An</u>	<u>Zr</u>
2024	---	4.5	0.6	1.5	---	---	---
7050	---	2.3	---	2.25	---	6.2	0.12
7075	---	1.6	---	2.5	0.3	5.6	---
6061	0.6	0.25	---	1.0	0.2	---	---

In addition to the surface oxide segregated particles which are rich in the alloy constituents can be found in the bulk as a result of quenching after heat treatment. Figure 3 contains electron micrographs with superimposed x-ray line scans of copper, iron, manganese, and aluminum showing these alloy constituent rich precipitates in 2024 aluminum. These inclusions could be potential sites for bond failure, especially if they are exposed to a high humidity environment at which corrosion could be initiated. They may also inhibit the effect of pretreatments such as anodization.

b. Adhesive

The processing of adhesives also is a multistep process in which a number of impurities, mainly alkali halides, are introduced as contaminants. Table IV lists some of the processing steps for epoxy adhesives and the impurities which can be introduced at specific steps during processing.

Although the epoxies are purified, residual amounts of NaOH and NaCl remain in the product. Analysis of four typical formulations (Table V) show that small amounts, from 5-70 parts per million (ppm), remain. While the effect of these hygroscopic impurities is unknown, Briggs, et al, have shown that small amounts of hygroscopic impurities can drastically affect the water absorption characteristics of elastomers⁵.

2.0 PREBONDING TREATMENTS

a. Metal or Alloy Adherends

Bonding "as received" materials such as the aluminum alloys nearly always results in poorly bonded weak structures. Consequently, some type of surface preparation is needed to make the adherend material more bondable. Usually the first step is to clean the surface, but not necessarily make it atomically clean. In some cases, the presence of foreign "atoms" may improve adhesion. Therefore, cleaning a surface

TABLE IV. POTENTIAL SOURCES OF IMPURITIES IN EPOXY RESINS

<u>Process</u>	<u>Common Impurities</u>	<u>Source</u>
Catalysis	Na, K	Caustic Soda
Prevent emulsification during washing	Na, S	Sodium hydrosulfite
Polymerization (special)	Li	Lithium hydroxide
Intermediate Production	B, F	Lewis acid Boron Trifluoride
Dehydrohalogenation	Na, Al	Sodium aluminate
Synthesis of ester	Na, K, Cl	Sodium or potassium salt of acid or acid chloride
Epoxidization	Cl	Hypochlorous acid, butylhypochlorite

TABLE V. IMPURITY ANALYSIS OF COMMERCIAL ADHESIVES (PPM)

	<u>Na</u>	<u>Cl (ionic)</u>	<u>Cl (total)</u>
EA9628	5	---	1700
FM123	20	---	500
AF55	70	140	680
PL729-3	50	---	---

for adhesive bonding means the modification of the surface region in a desirable way⁶. Care must be taken using processes that include numerous steps that one step does not negate a previous step, for example, the final step of an aluminum alloy treatment may include preparation of a well defined oxide layer by anodization or other chemical methods. If this surface were then exposed to a long hot water wash, the oxide character would be changed. Consequently, it becomes extremely important that the surface be characterized after each step.

In dealing with aluminum alloys, the first step for bonding preparation is to remove the original magnesium rich oxide surface layer. This can be accomplished by mechanical or chemical methods or both. Listed in Table VI are some of the commercial and non-commercial chemical treatments investigated. These treatments include a simple degreasing to highly reactive alkaline and acid etching. Figure 4 contains Auger spectra along with corresponding in-depth profiles from three chemically treated 6061 alloy specimens. The first was treated with NaOH followed by HNO_3 -HF; the second was treated with NH_4HF_2 ; and the third was treated with the commercial etch solution alodine, a conversion coating mixture of phosphoric acid, chromic acid, and NaF. In each case, the different effects on the surface composition in terms of the alloy constituents and chemical solutions are evident. The corresponding in-depth elemental profiles show the effect of the three chemical treatments on the oxide thickness.

Similar Auger data was obtained from the other three pretreated alloys. When combined with ISS and SIMS data from the same surfaces a very informative matrix of surface elemental information can be constructed. Table VII is an example of one such matrix showing a simple qualitative comparison between the chemical treatments on 7075 aluminum. The first four columns reflect the elements present in the bulk alloy and the last three are the elements found in the various chemical solutions.

TABLE VI. SURFACE CHEMICAL TREATMENTS FOR ALUMINUM ALLOYS

ID Number	Description	Treatment
1.	Degrease	Metal sample slurried in acetone, wiped dry, then ultrasonically cleaned in carbon tetrachloride for 5 minutes.
2.	Alkaline	Metal sample submerged in 0.1N sodium hydroxide, room temperature for 2 minutes.
3.	ALK + HNO_3/HF	Treatment #1 followed, then sample submerged in a solution of 170 ml nitric acid, 30 ml hydrofluoric acid, 800 ml distilled water, room temperature for 2 minutes.
4.	HNO_3/HF ALK + FPL	Acid solution. Treatment #1 followed, then sample submerged in a solution of 30 g sodium dichromate, 300 g sulfuric acid, distilled water to make one liter, 50°C for 5 minutes.
5.	FPL	Dichromate solution as described in #4.
6.	NH_4HF_2	Metal sample submerged in solution of ammonium bifluoride (10 g/liter) room temperature for 2 minutes.
7.	Alodine	Metal sample submerged in solution of 65 g phosphoric acid, 10 g chromic acid, 5 g sodium fluoride, distilled water to one liter, 50°C for 2 minutes.

TABLE VII. MAJOR ELEMENT DETECTED AT THE SURFACE OF
7075-T6 ALUMINUM BY ISS (I), SIMS (S)
AND AES (A)

Surface Treatment	Al	Cu	Mg	Zn	Cr	P	F
Degrease	I _S A		I _S A				
Alkaline	I _S A	I _S A	I _S A	A			
ALK + HNO ₃ /HF	I _S A	I _S A					I _S A
HNO ₃ /HF	I _S A	I _S A	S				I _S A
ALK + FPL	I _S A				S _A	A	
FPL	I _S A				S _A	A	
NH ₄ HF ₂	I _S A		I _S A				I _S A
Alodine	I _S A			I _S A	I _S A	A	

Figure 5 shows the + SIMS spectra from 2024 Al in which the surface was only degreased and not etched. This surface is composed primarily of oxidized magnesium which provides good initial bondability but very poor long time durability. The degradation of the interphase with moisture ingress apparently proceeds due to the magnesium instability. Also shown is the SIMS spectrum following heating of this degrease surface with the accompanying increase in Na compared with Al + and other ions. This increase of alkalis apparently occurs due to grain boundary migration from the bulk and will be mentioned later.

A common method of cleaning a surface is to use some type of abrasive such as abrasive paper or grit blast. The advantage of abrasion in terms of adhesive bonding is the increase in surface roughness and thus an increase in the bond strength simply because of the increase in the number of sites for the "hook and latch" effect between adherend and adhesive. Figure 6 contains two positive secondary ion mass spectra from the surfaces of an "as received" and grit blasted (sand) 6Al-4V-Ti alloy. The grit blasting did remove some of the sodium but left behind an aluminum and silicon rich surface due to the impact of the sand grit particles. Their presence on the surface could offset the roughening advantages of grit blasting since they are possible sites for bond failure, either the result of poor adhesive wetting or just the fact that the loose grit particles do not adhere very well to the alloy surface.

Some of these surface pretreatments were used for years to condition aluminum and titanium alloys for bonding and the resulting bonds were generally good in terms of strength. In aircraft applications strength as well as long term reliability and durability are important considerations. Consequently, new and better surface preparations were investigated which would not only result in stronger bonds, but also offer corrosion protection.

Anodization was introduced as a surface treatment since the growth of the anodic oxide film could be precisely controlled and the anodized aluminum alloys were more resistant to corrosion since anodization leaves a surface oxide free of the alloying constituents such as copper and magnesium if the proper anodization conditions are chosen.

Again a matrix of surface characterization data was generated to show, for example, the effects of the various electrolytes and anodization conditions (i.e., voltage, concentration and temperature) on the alloy surface. As in the case of the chemical treatments, chemical species of the electrolytes are usually detected on anodic oxide surfaces. The Auger spectra from ammonium chromate and phosphoric acid anodized aluminum showing the presence of chromium and phosphorous from the respective electrolytes. The concentration and depth distribution of these species appears to vary with electrolyte and anodization conditions. Also, the chemical states may differ on the surface compared with the bulk oxide.

Figure 7 contains three Auger spectra from three NH_4HF_2 pretreated 2024 aluminum panels which were anodized at 10V for 15 seconds, 35 seconds, and 60 seconds in $1.0\text{M}\text{H}_3\text{PO}_4$. An interesting observation in these spectra is the decreasing amounts of magnesium and phosphorous with anodization time. In-depth profiles of the respective oxide layers show that both magnesium and phosphorous are present only within a few monolayers of the surface and that the oxide thickness increases with time. The in-depth elemental profile of the 35 second anodized 2024 alloy in Figure 8 shows that copper, which is not detected on the surface, is present at the oxide metal interface at higher concentrations than in the bulk which may be the cause of observed defects (pits) on the anodized surface.

During chemical treatments or anodization, alloys containing copper, manganese, or silicon are highly susceptible to the formation of smut on their surfaces. The condition usually develops when certain alloys such as 2024 aluminum are etched in sodium hydroxide or other solutions. This is a significant problem in large commercial chemical treatments or anodization baths containing thousands of gallons of chemical solutions which cannot be economically replaced after each use, even though they contain significant amounts of dissolved impurities such as copper. Figure 9 contains SEM micrographs of a copper rich smut material formed on 2024 aluminum by electroless deposition in a chemical etching bath of hot sulfuric-chromic acid for a prolonged time. The micrograph on the right shows what the surface should look like if a shorter etching time is used. One method to remove the smut is to simply physically wipe it off when still wet. Although the wiped surface may appear to be clean, ISS spectra in Figure 10 from a smutted surface, which was wiped, still shows excess copper remaining. Since the particles shown in the SEM micrograph are soft and can be smeared into the rough porous cavities, the presence of copper after wiping is not too surprising. Similar smutting primarily due to copper is shown in Figure 11 where a Ti adherend given an acid etch showed smutting. Although the Ti contained no alloying elements associated with smutting, it developed that the etch had been used previously to etch 2024 Al and contained copper from these etchings. Therefore, attention must be given to the cleanliness of processing solutions.

A similar smutting contamination is observed during anodization in which the electrolyte bath contains dissolved copper. The copper may be deposited on the cathode and change the electrical characteristics of the anodized bath. After the current is removed from the electrolyte bath, the copper may go back into solution. If the workpiece is then held in the bath

for a period without being removed, copper may form on the surface of the anodized film. This copper rich layer then may form a weak boundary layer when the material is adhesively bonded. Figure 12 shows evidence of this contamination effect from an anodizing bath. The cathode piece was aluminum while the anode was 2024 aluminum. The ISS spectra of the aluminum cathode in Figure 12 shows that copper had gone into solution and plated out on the cathode surface while the anodized 2024 aluminum surface was void of copper.

The examination of both anodes and cathodes using SIMS and ISS show that contamination of both the anode and the cathode occur under certain circumstances. Failure to remove the workpiece following anodization can create contamination in the anodized coating. Dissolution of the lead cathode could cause problems in anodization of aluminum when using lead tanks. Whether deleterious to the coating or not, these results indicate that the anodization process is an ever changing system, and is not surprising that problems in reproducibility have been encountered. Likewise, it is not surprising that one laboratory to another has had difficulty in reproducing the same chemistry and morphology of anodized films. Figures 13 and 14 show ISS/SIMS results for the anode and cathode, respectively, from a H_3PO_4 electrolyte. The composition of both anode and cathode are seen to change during the anodization cycle.

Allen and Alsalim⁷ showed that it is essential that smut be removed because its presence on surfaces to be bonded reduces bond strength by about 50 percent. They found in their work on martensitic base stainless steels that all the treatment solutions which effectively attack the steel leave a deposit of what they termed graphite on the surface. It seems unlikely that smut produced by Allen and Alsalim consists only of carbon, particularly in the graphite form because the alloy they used contains significant amounts of other materials which show serious smutting characteristics such as silicon, manganese, and copper.

Chemical treatments such as acid pickling on stainless steels frequently leave behind more contamination than was originally present. This contamination can be deleterious to the use of stainless steels in such applications as adhesive bonding. This chemical residue that is left behind following treatments such as acid pickling is usually called smut. Smut is formed on 304 stainless steel by treatment in sulfuric acid. The smut formed on the stainless steel is characterized primarily by ion scattering spectrometry (ISS) and secondary ion mass spectrometry (SIMS) as shown in Figure 15. It was found that the majority of the smut formed on 304 stainless steel was not carbon or graphite but rather silicon in an oxidized form⁸. This silicon rich smut was effectively removed by a further chemical treatment with sulfuric acid and chromic acid, a similar mixture to that often used for cleaning glass. This cleaning procedure is shown by surface chemical analysis methods to produce a clean surface comparable to that obtained by abrasion.

b. Graphite Fibers

The problem of surface chemistry alterations resulting from prebonding treatments is not limited to metal adherends. To enhance adhesion between graphite fibers and a polymer matrix the fibers can also be subjected to pretreatments, such as oxidation. Unfortunately, as Drzal⁹ reported, an increase in the amount of material that can be desorbed with moderate thermal treatment, such as curing, can result. Figure 16 contains the Auger spectra from an "as received" untreated fiber and one which underwent a manufacturers proprietary treatment. The spectrum from the treated fiber shows that the fiber was oxidized. However, during the process it picked up S, N, Cu, and Na. These species have the potential to affect the interaction between the fiber and polymer matrix.

3.0 ENVIRONMENT

The third category of potential contamination sources for adhesive bonding materials is environmental exposure. This includes atmospheric exposure and material handling. Impurities chemisorbed or physisorbed, either into the bulk or on the surfaces, from the atmosphere, especially during heat treatments, may drastically influence the mechanical properties of metal adherends. Table VIII shows that the general effect on 2024 aluminum with exposure to SO_2 and water vapor (high humidity or steam) decreases in tensile strength and elongation.

After the adherend materials are received and prepared for bonding, handling becomes an important consideration since the panels are usually moved from pretreatment facilities to bonding facilities or stored until needed. Figure 17 shows Auger spectra from phosphoric acid anodized 7075 aluminum, a panel of the anodized 7075 wiped with a paper usually placed between anodized panels for storage, and an anodized panel wiped with a clean cotton glove. There are two noticeable changes in the surfaces of the wiped panels compared to the original. In both wiped panels there is a noticeable increase in the alloying elements magnesium and zinc along with the presence of carbon. An additional effect of wiping, which may not be classified as a contaminant, but nevertheless potentially deleterious to bond strength and durability, was the smearing of the fragile oxide layer, defeating one of the purposes of anodization, namely, to produce a porous oxide with a uniform known thickness. Figure 18 contains the oxygen in-depth concentration profiles of the original anodized 7075 aluminum and two wiped panels. The profiles show a decrease in the oxide film thickness as a result of the wiping. Bonded specimens of the wiped panels failed at the interface of the adherend and adhesive.¹⁰

One of the tests for determining bond strength and durability of the adhesive is the wedge test in which a wedge

TABLE VIII. EFFECT OF IMPURITIES IN HEAT TREAT
ATMOSPHERES ON MECHANICAL PROPERTIES
OF 2024-T4 ALUMINUM ALLOY SHEET (Ref 2)

	<u>Tensile Strength % Decrease</u>	<u>Elongation % Decrease</u>
Dry air containing 0.0002% sulfur dioxide (a)	3	27
Air containing 25% combustion products from natural gas (b)	5	75
Dry air containing 0.0012% sulfur trioxide (c)	7	35
Air containing 0.8% water vapor (40 F dew point) (a)	8	40
Dry air containing 0.007% sulfur dioxide (a)	15	68
Sulfur dioxide (a)	20	64
Air containing 3.4% water vapor (80 F dew point) (a)	25	77
Moist oxygen (a)	29	82
Ammonia (a)	29	82
Water vapor (100% saturated steam) (a)	60	95

(a) Heated at 920 to 930 F for 20 hr.

(b) Heated for 2 hr.

(c) Heated for 30 min.

is driven into the bond joint creating an initial crack within the adhesive. The wedge test is illustrated in Figure 19. The specimen is then exposed to some environment such as high temperature and humidity and monitored for crack growth rate and length.

The photograph on the right in Figure 15 shows the exposed surfaces of an adhesively bonded structure that failed adhesively during a wedge test in a SO_2 environment. Prior to bonding, a piece of adhesive tape was placed with the oxide surface at Point A and then removed. After bonding, this specimen and one which was not exposed to the tape, were placed in a SO_2 environment to characterize the effects of a high SO_2 atmosphere on the bond using the wedge test. The specimen that was not exposed to the tape failed cohesively, while the tape exposed specimen failed cohesively to the tape exposed area where failure became 100% adhesive and total delamination resulted. The Auger spectra to the left in Figure 20 show chlorine present on the exposed surface of the adhesive which was in contact with the oxide surface. Analysis of the adhesive tape shows it to contain lithium chloride. The exposure of this surface to the adhesive tape probably resulted in poor wetting by the bonding adhesive and thus poor bonding. Again, the implication of the results from this example is the potential effects of improper handling of the adherend, especially with bare hands or dirty gloves.

As previously stated, most adhesives used in aircraft applications are thermosetting epoxies with cure temperatures ranging from 250°F to 350°F . At these temperatures surface migration of certain bulk impurities which were introduced during processing was observed. Figure 21 contains positive ion SIMS spectra of an anodized 6Al-4V-Ti substrate at room temperature (156-1) and after it had been heated to 350°F , a typical cure temperature for bonding titanium. Heating has resulted in an increase in sodium and the alloying element

aluminum, which probably occurs by grain boundary diffusion to the surface and is quite common in many alloys.

Also, as mentioned earlier, the adhesive can contain a number of impurities and at elevated cure temperatures these impurities can migrate to the interphase region. The positive ion SIMS spectra from a room temperature and 250°C cured epoxy in Figure 22 show a very large increase in sodium and potassium at the 250°C cure temperature. Analysis of such adherend and adhesive materials which were bonded and subsequently failed at high humidity and elevated temperatures indicate early crack propagation at the adhesive-oxide interface. Large amounts of impurity ions such as sodium and potassium are usually present in this region. At elevated cure temperatures the very mobile ions such as lithium, sodium, and potassium become concentrated at the interphase. Then, if the conditions for bond failure under water attack are those for hydrolysis, the diffusion of alkali ions to the interphase region would increase the osmotic potential and enhance the destructive ingress of water at the interphase.

Finally, the bonding environment itself can be a source of contamination. The large panels bonded for aircraft applications are cured in autoclave chambers. The specimens to be bonded are usually covered with a sealed bag which is evacuated with a roughing pump. The backstreaming gases from the pump and the outgassing components from the bag during the cure cycle are high in carbon, chlorine, and sulfur. These contaminants can be introduced to the interphase region of the bond joint at or near the structures' edges.

Certain elements are more deleterious to adhesive bonding than others. Some are especially to be avoided due to the formation of weak boundary layers. Fluorine has been shown to produce such failures in the weak boundary layer in aluminum alloys.¹² Work in this laboratory shows that anodization of the valve metals, titanium, tantalum, and tungsten produces an

anodized film, which may easily be stripped from the surface.¹³ Virtually any thickness of oxide may be obtained by anodizing first in an electrolyte containing fluorine, and then continuing to anodize in a conventional electrolyte. Fluorine remaining on the surface, following stripping of the oxide, causes a weak boundary layer to exist even upon a second anodization with an electrolyte not containing fluorine. Initial H₂O contact angles on the failure surfaces showing fluorine were very low, and rapidly spread to zero. Peel tests on specimens etched over the entire specimen and then anodized over one half the specimen in an electrolyte containing fluorine gave peel results as shown in Figure 23. Following testing the failure surfaces were found to contain large amounts of fluorine as shown in the elemental profile with depth seen in Figure 24. Such profiles establish, beyond a doubt, the locus of failure.

SECTION III

CONCLUSIONS

The surface composition of candidate materials for adhesively bonded structures could be significantly different from the bulk due to contamination introduced during raw material processing, bonding pretreatments, and environmental exposure. Variations of composition and the appearance of certain elements at the interphase can be all important in the bondability and long-term durability of adhesive bonds. A major research problem which tends to keep adhesive bonding in the realm of a "black magic" art instead of an exact science is the lack of mechanical and environmental tests which are sensitive to small variations in surface chemistry. Consequently, further research is needed to design tests whose statistical variations are small enough to show the effects of controlled surface composition changes as well as the presence of unexpected contamination.

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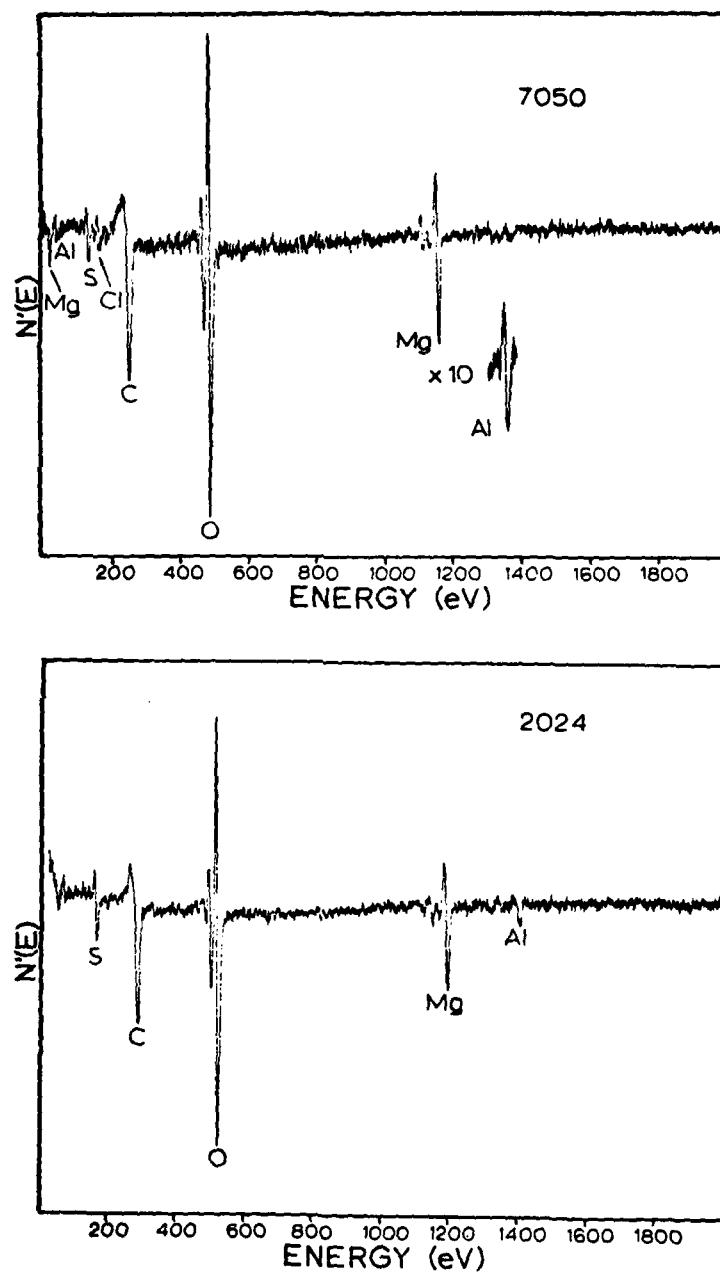


Figure 1. Auger Electron Spectra from "As Received" 7050 Al and 2024 Al Alloy Sheets

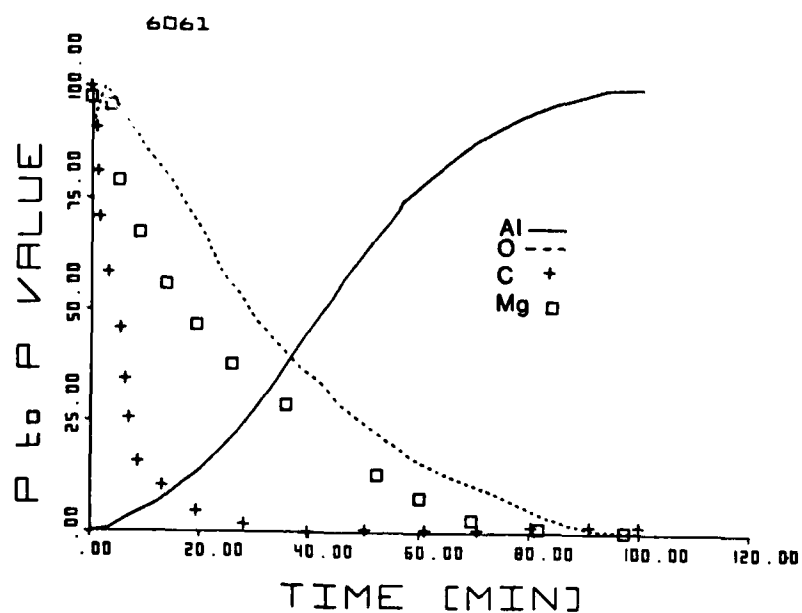
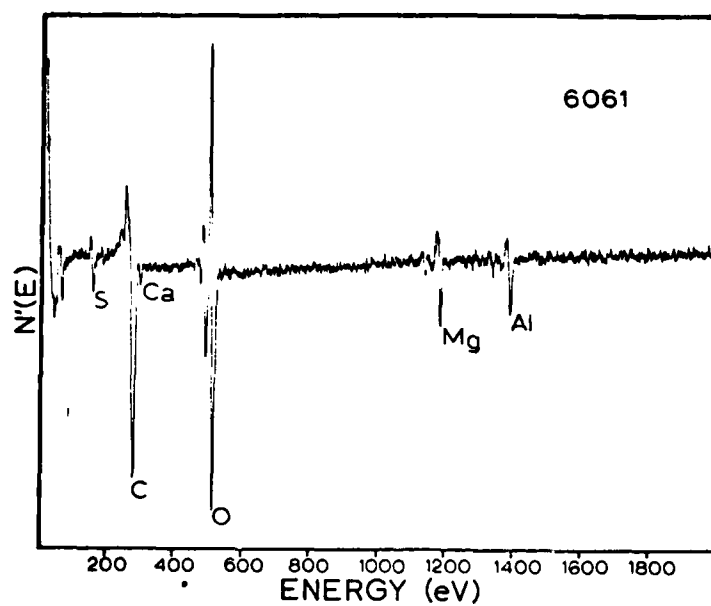
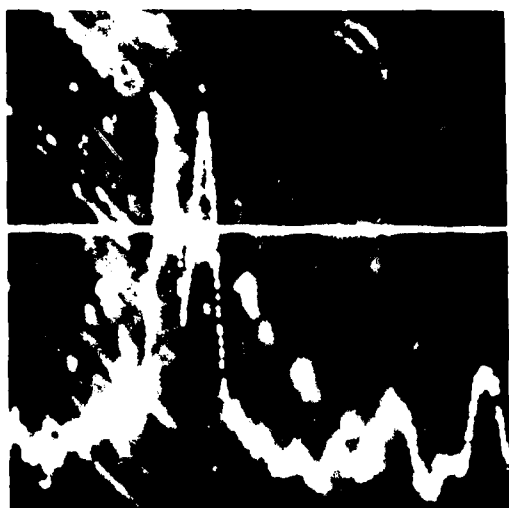
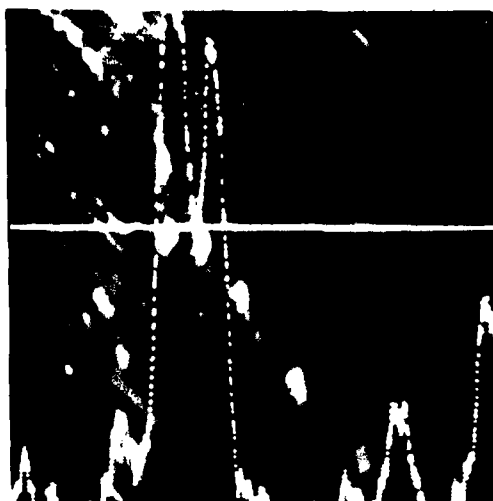


Figure 2. Auger Electron Spectrum and Elemental In-depth Elemental Profiles for Al, O, C, and Mg from an "As Received" 6061 Al Alloy Sheet

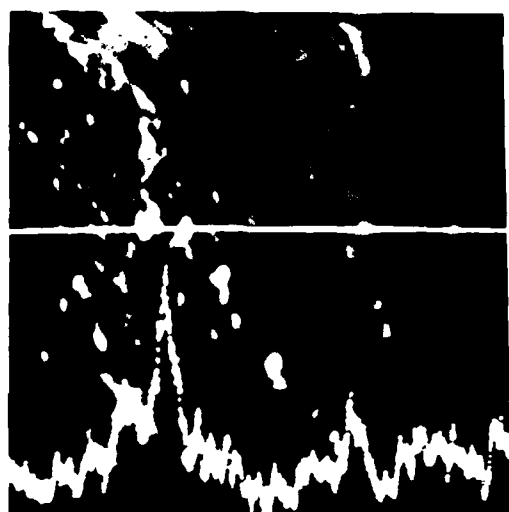
2024-O (360X)



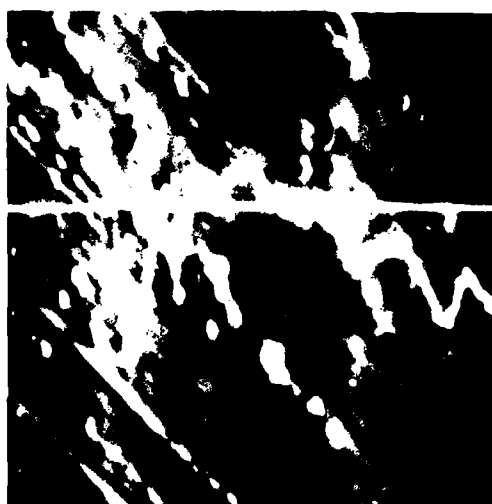
Cu



Fe



Mn



Al

Figure 3. Backscattered Electron Images at 360X Magnification from a Polished 2024 Al Sheet with Superimposed X-ray Line Scans of Cu, Fe, Mn, and Al

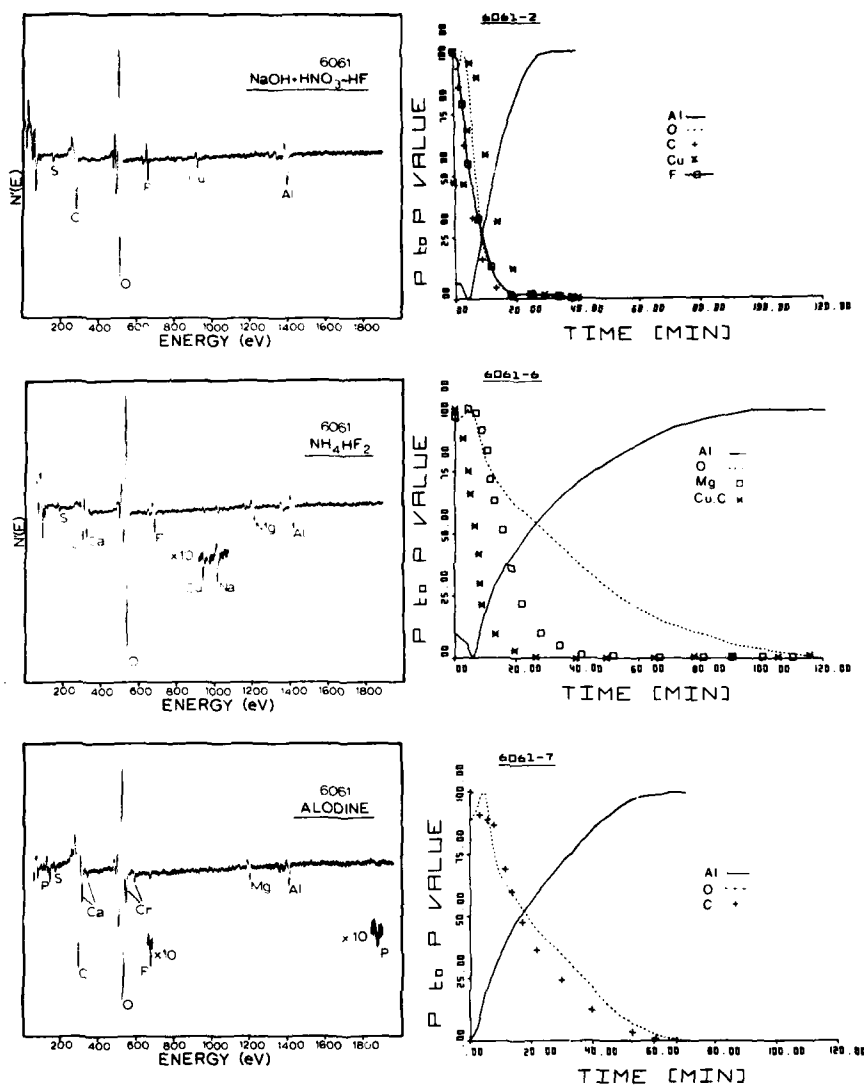


Figure 4. Auger Electron Spectra and In-depth Elemental Profiles from Chemically treated 6061Al Alloy Sheets

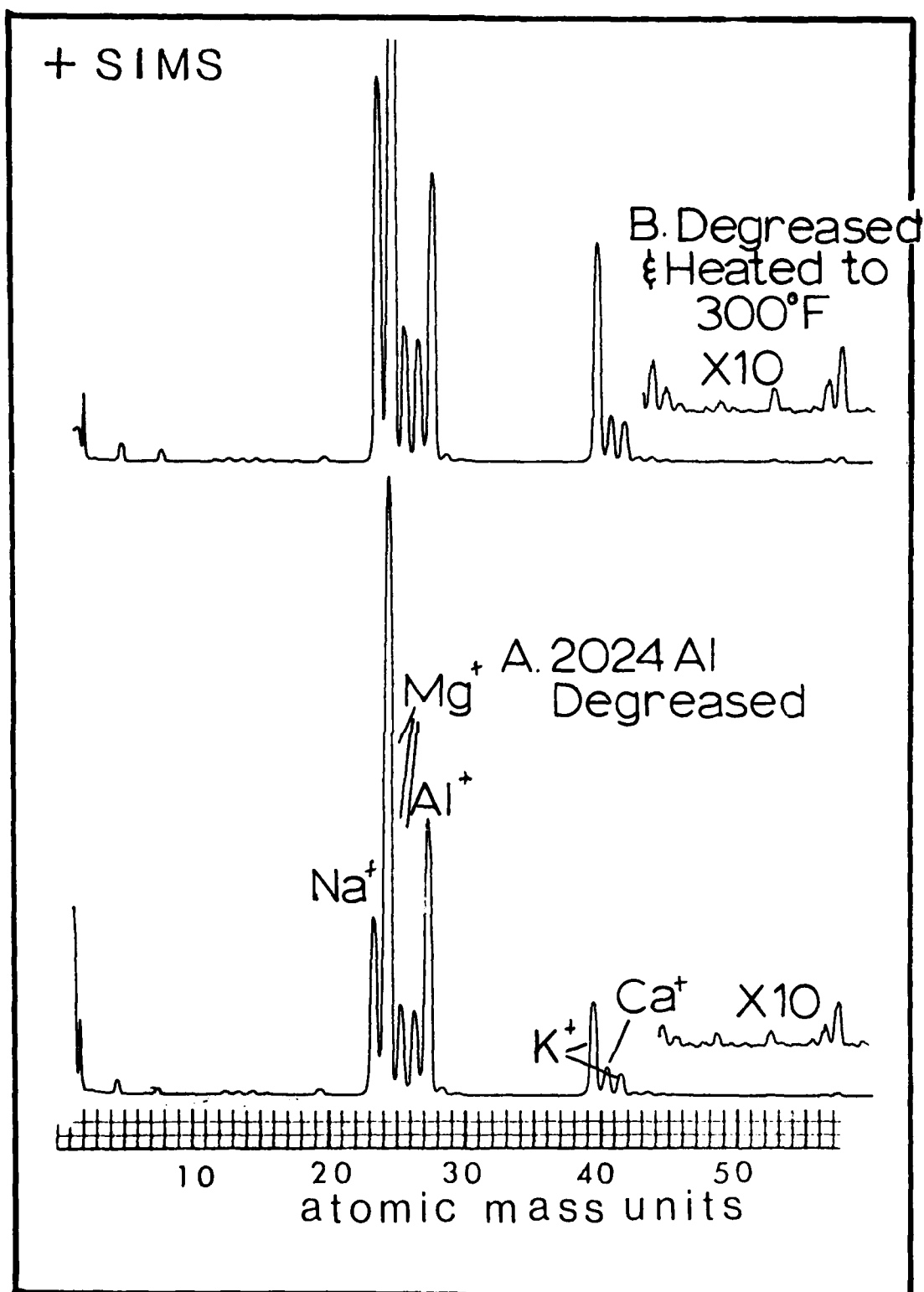


Figure 5. + SIMS Spectra of 2024 Aluminum Alloy

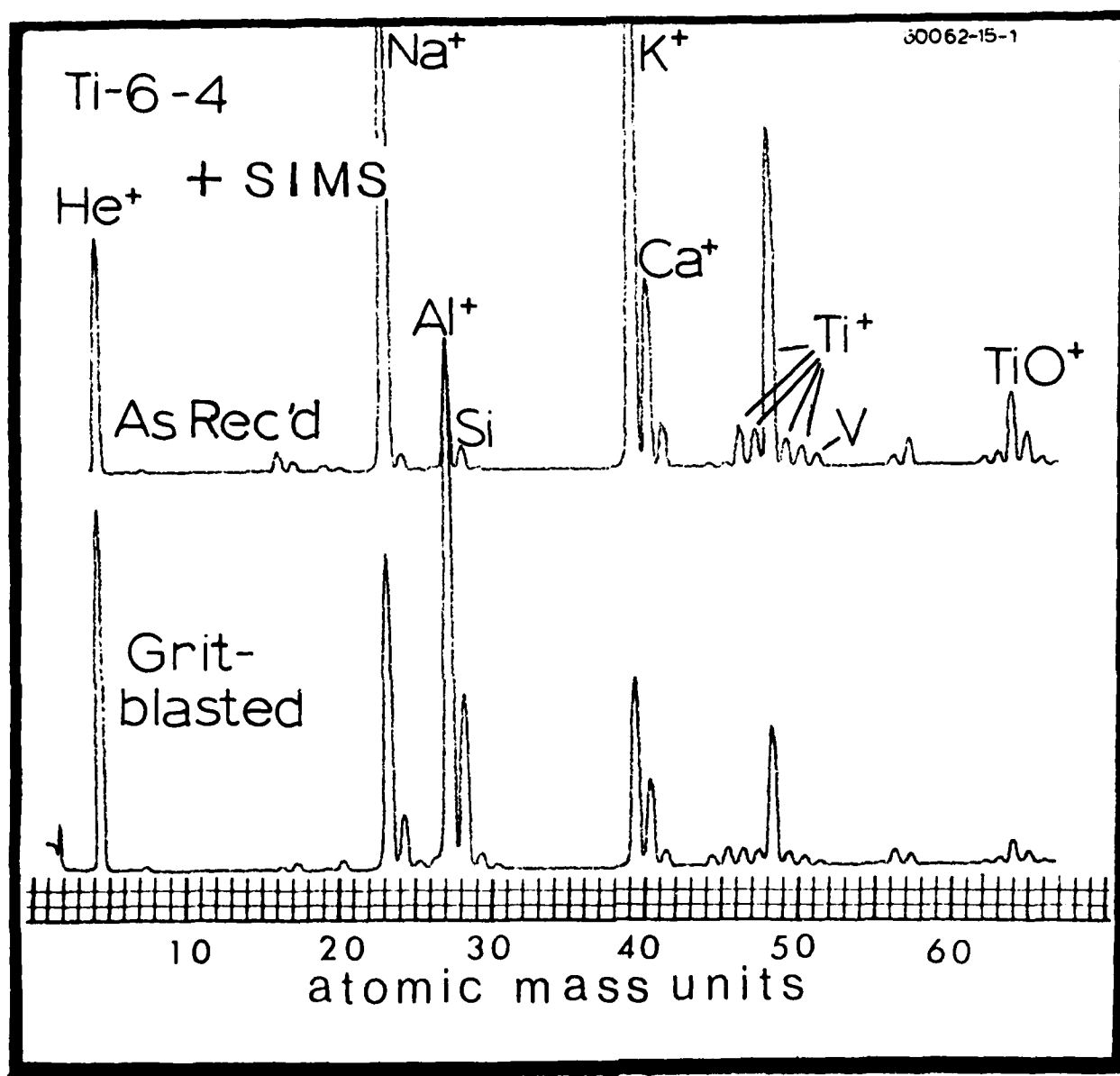


Figure 6. Positive Secondary Ion Mass Spectra from "As Received" and Grit Blasted 6Al-4V-Ti

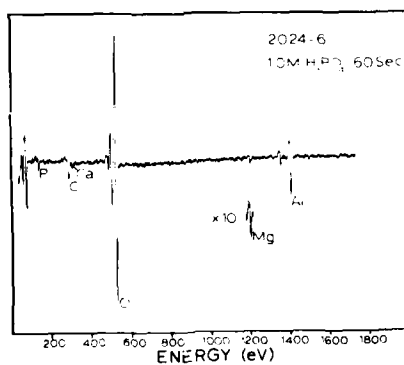
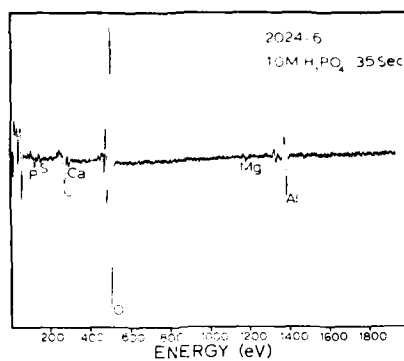
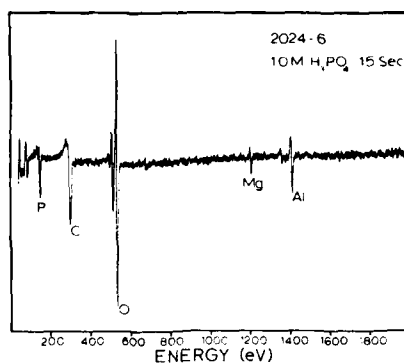


Figure 7. Auger Electron Spectra from 2024A1 Sheets Anodized in 1.0M H_3PO_4 for 15, 35, and 60 Seconds

2024-6 1.0M H₃PO₄ 10V 35 SEC

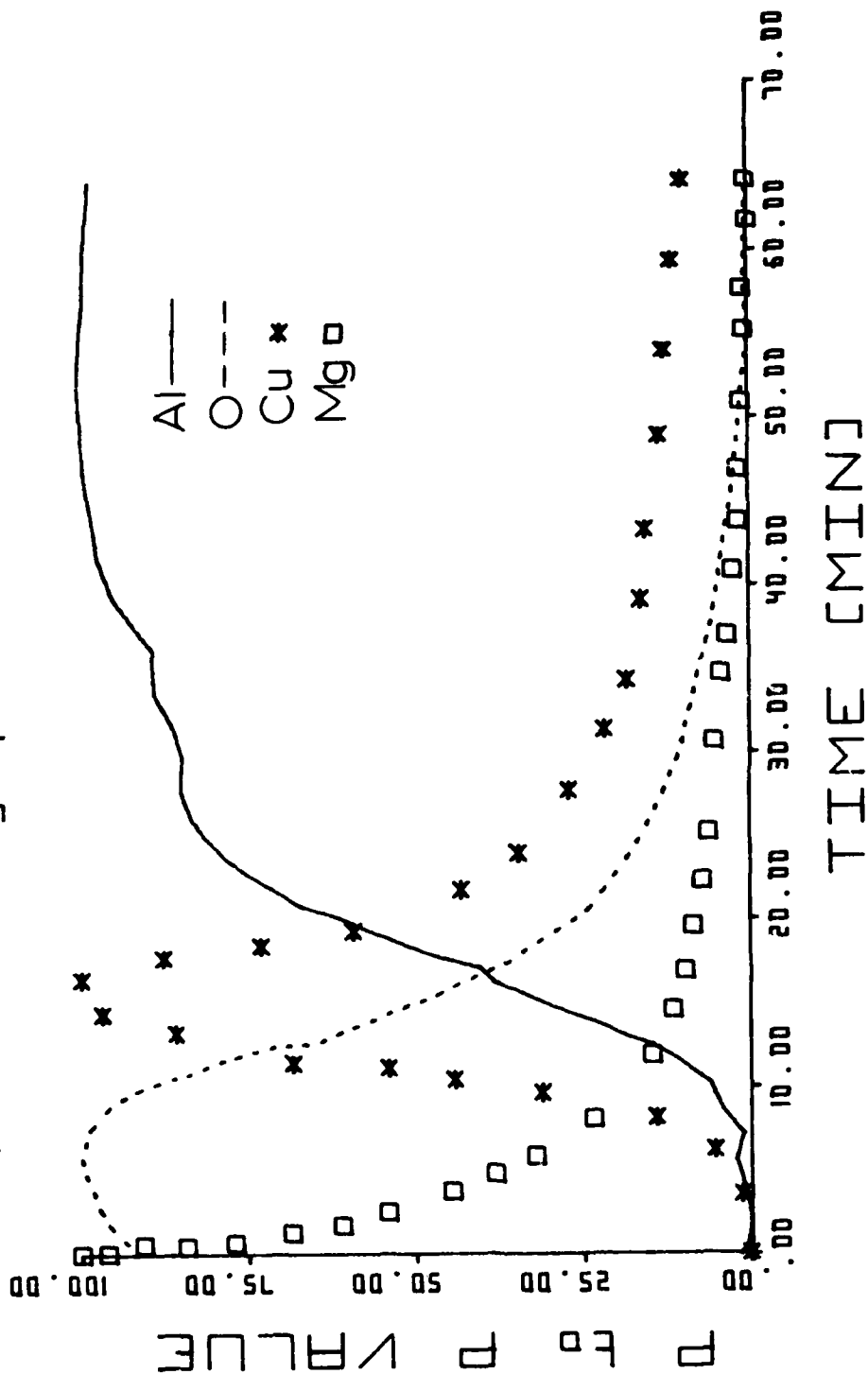


Figure 8. Auger In-depth Element Profiles for Al, O, Cu, and Mg from an 1.0M H₃PO₄ 10V 35 Second Anodized 2024Al Sheet

2024T3



SMUT

4460X



CrO Stripped

Figure 9. Scanning Electron Micrographs at 440 X Magnification of Smutted Surface and Properly Etched Surface of 2024 Al Etched in Hot Chromic-Sulfuric Acid

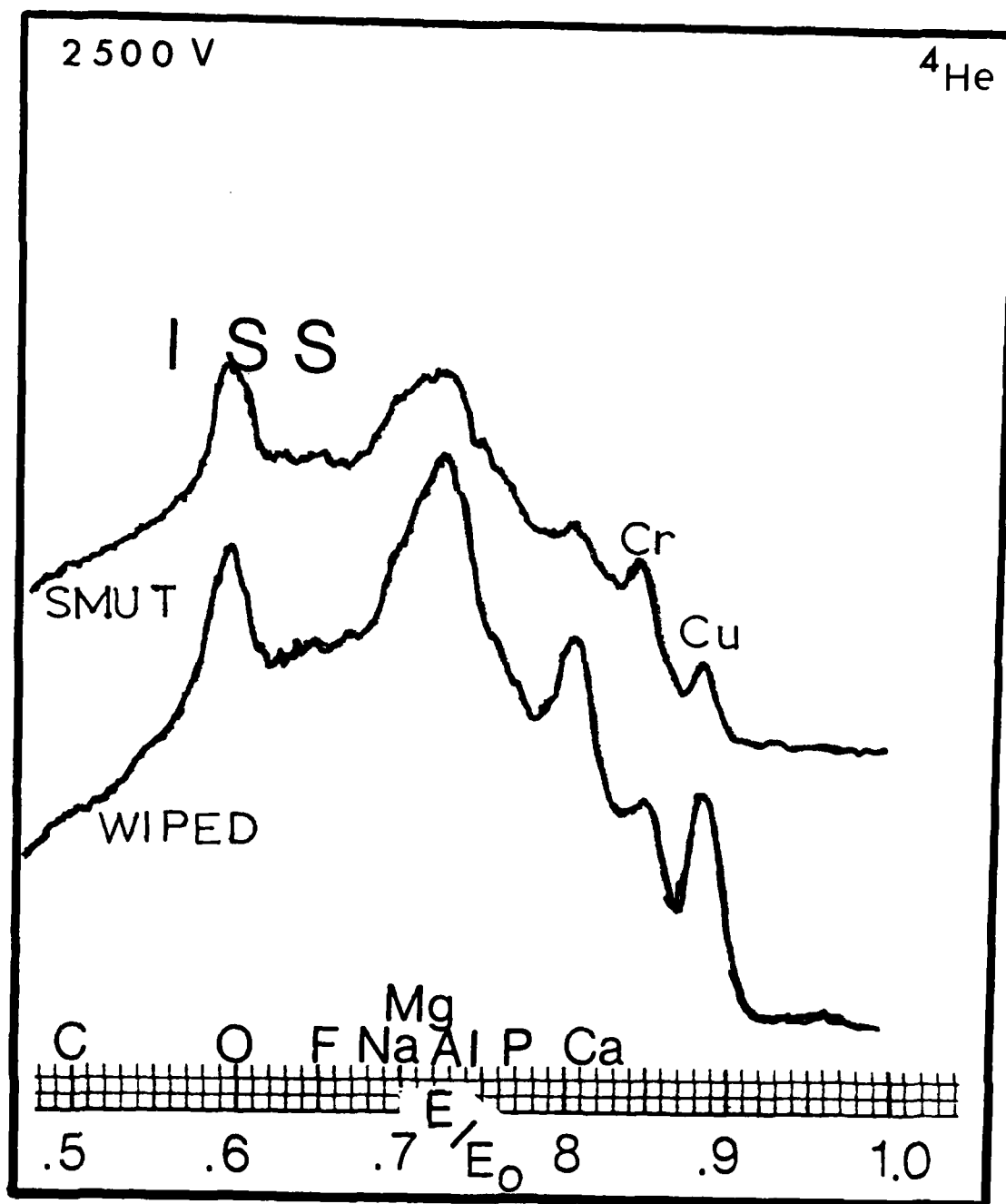


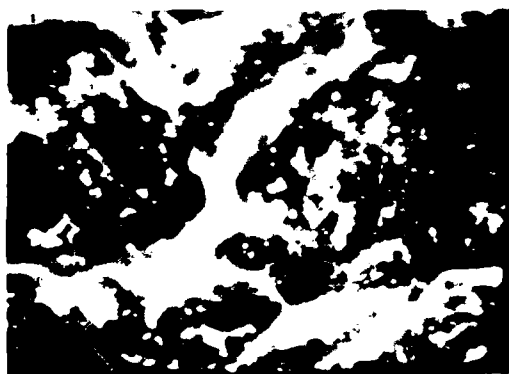
Figure 10. Ion Scattering Spectra from the Smutted Surface Shown in Figure 8 and from the Same Surface After Wiping

Ti c p



3 a

5 μ m



3 b

Figure 11. Scanning Electron Micrographs from Ti (C.P.) Etched in Fresh Solution (3a) and in Used Solution Containing Dissolved 2024 Aluminum

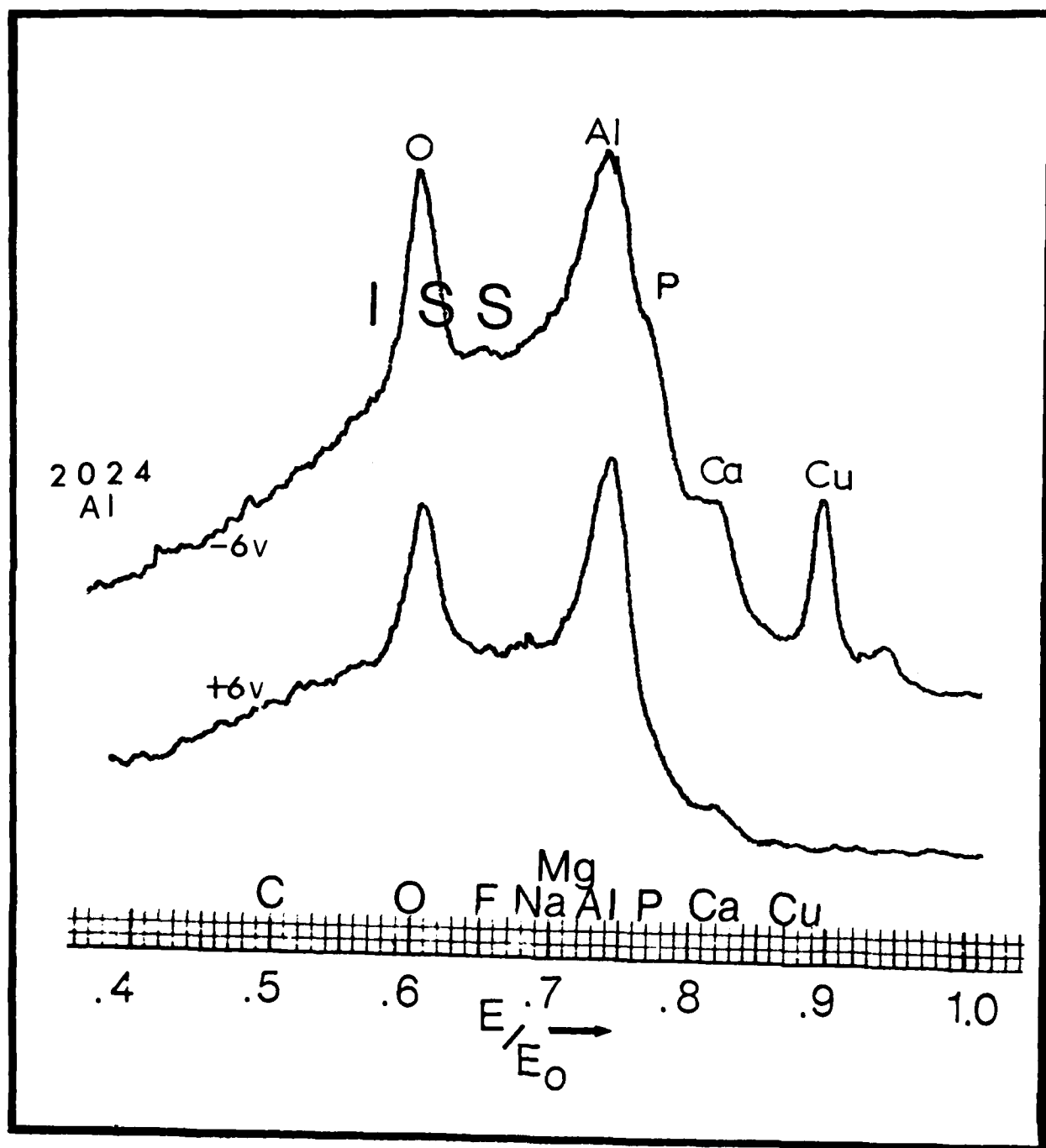


Figure 12. Ion Scattering Spectra from an Al Cathode (-6V) and 2024Al Anode (+6)

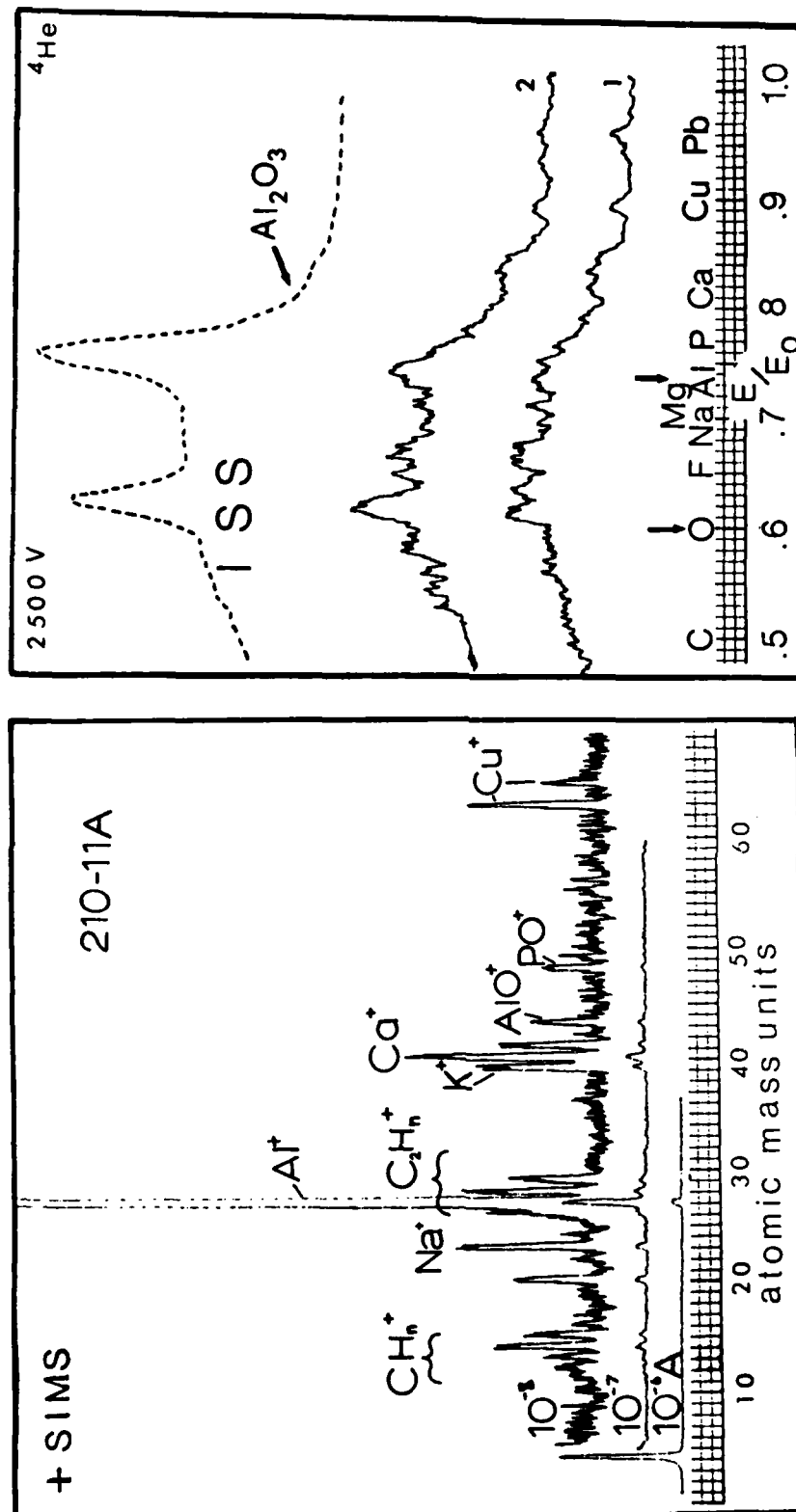


Figure 13. ISS/SIMS Data for 2024 Aluminum Anode from H_3PO_4 Electrolyte

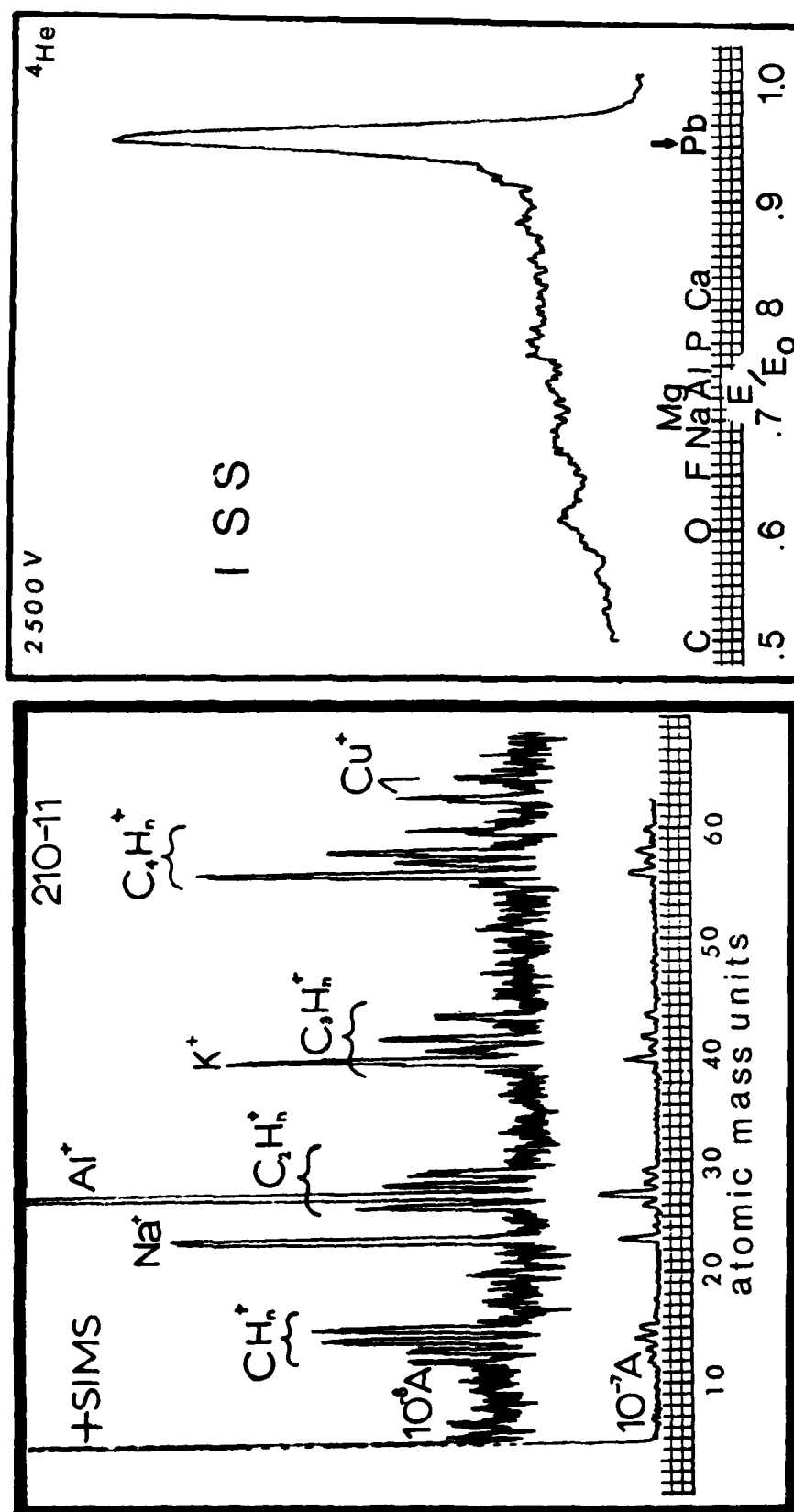


Figure 14. ISS/SIMS Data from Corresponding Pb Cathode from H_3PO_4 Electrolyte

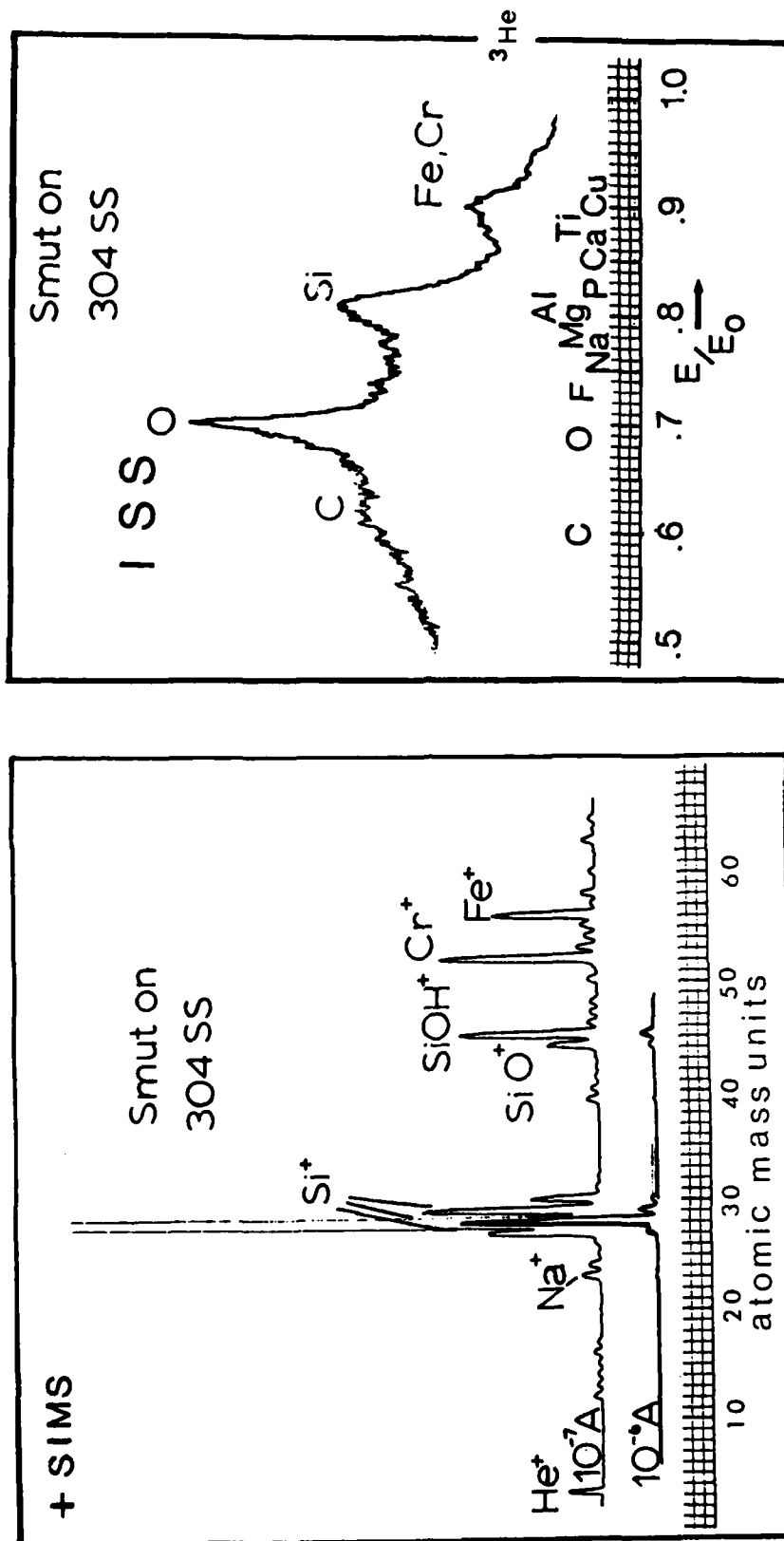


Figure 15. ISS/SIMS Data for Smut on 304 Stainless Steel

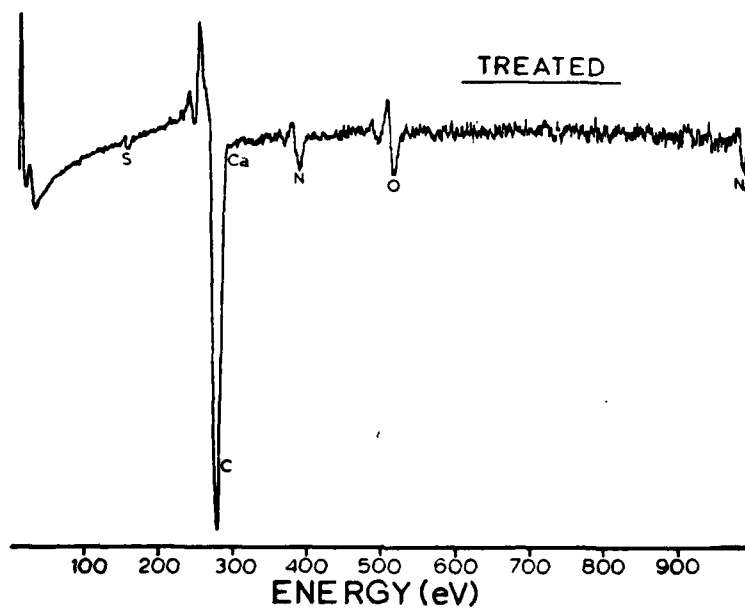
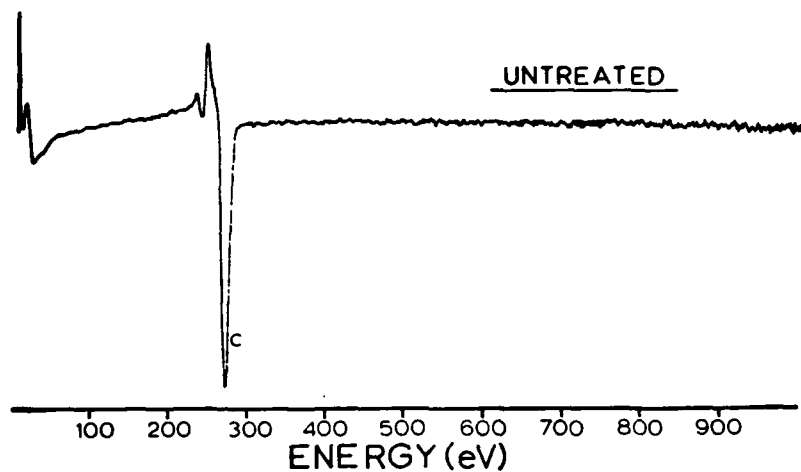


Figure 16. Auger Electron Spectra from Untreated and Treated Graphite Fiber

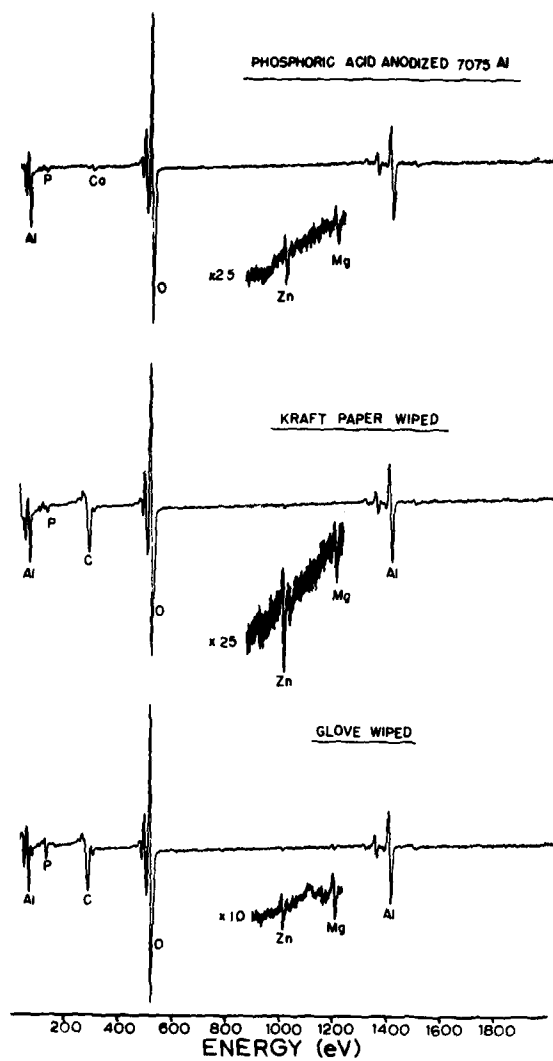


Figure 17. Auger Electron Spectra from Phosphoric Acid Anodized 7075Al, an Anodized 7075 Panel Wiped with Kraft Paper and an Anodized 7075 Panel Wiped with a Cotton Glove

OXYGEN PROFILES

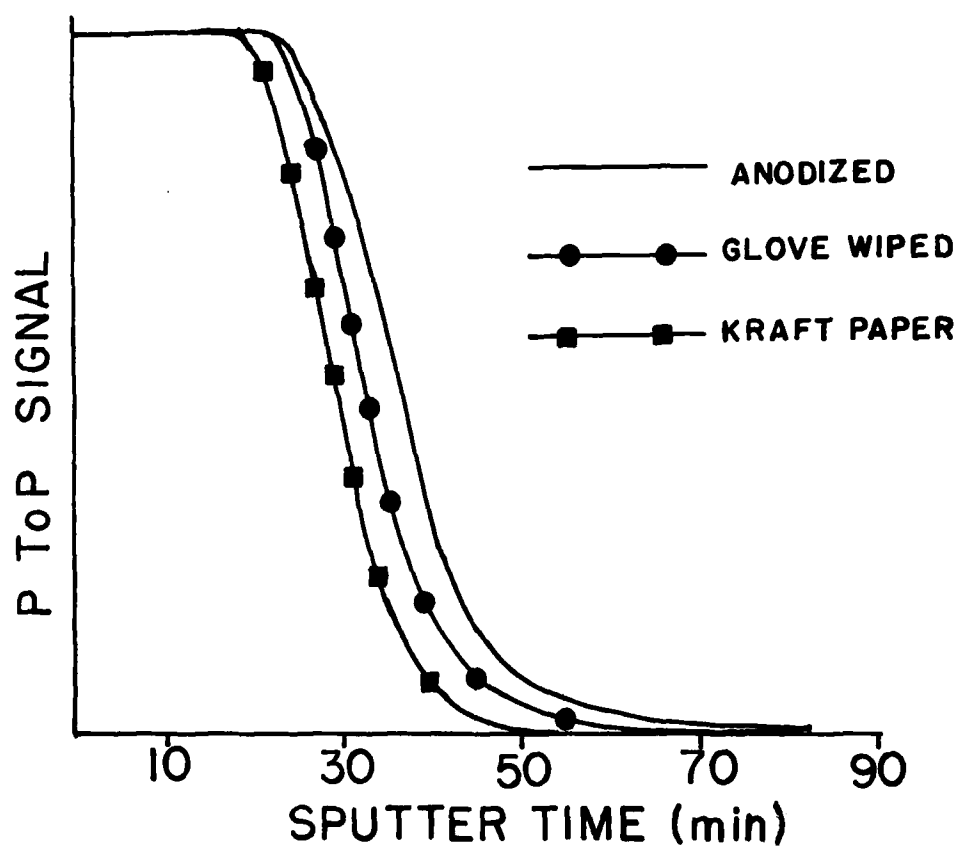


Figure 18. Oxygen In-depth Profiles from Phosphoric Acid Anodized 7075 Al "as is", Kraft Paper Wiped, and Glove Wiped

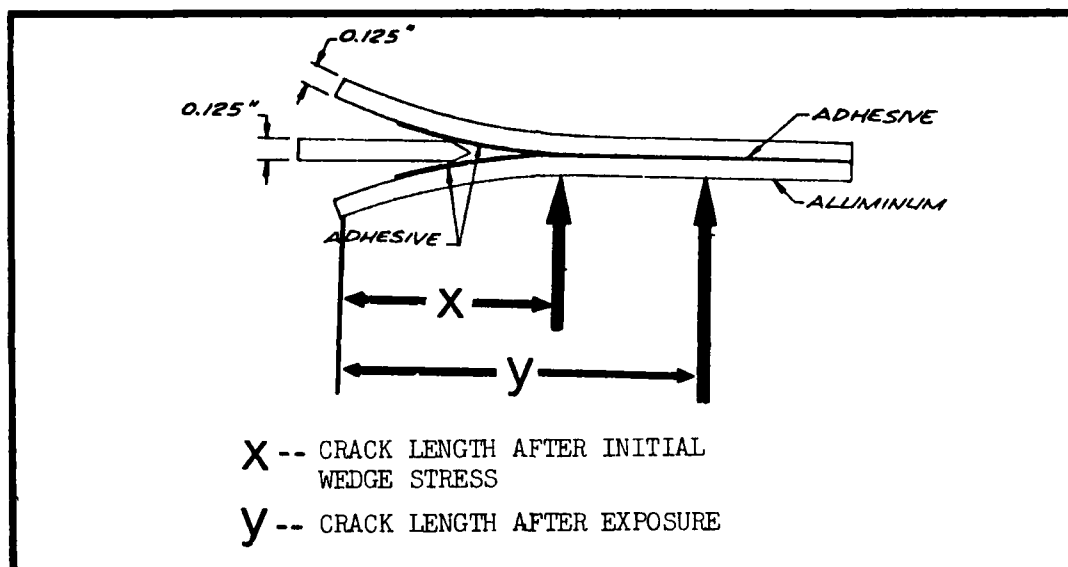


Figure 19. Illustration of the Wedge Test for Adhesively Bonded Structures

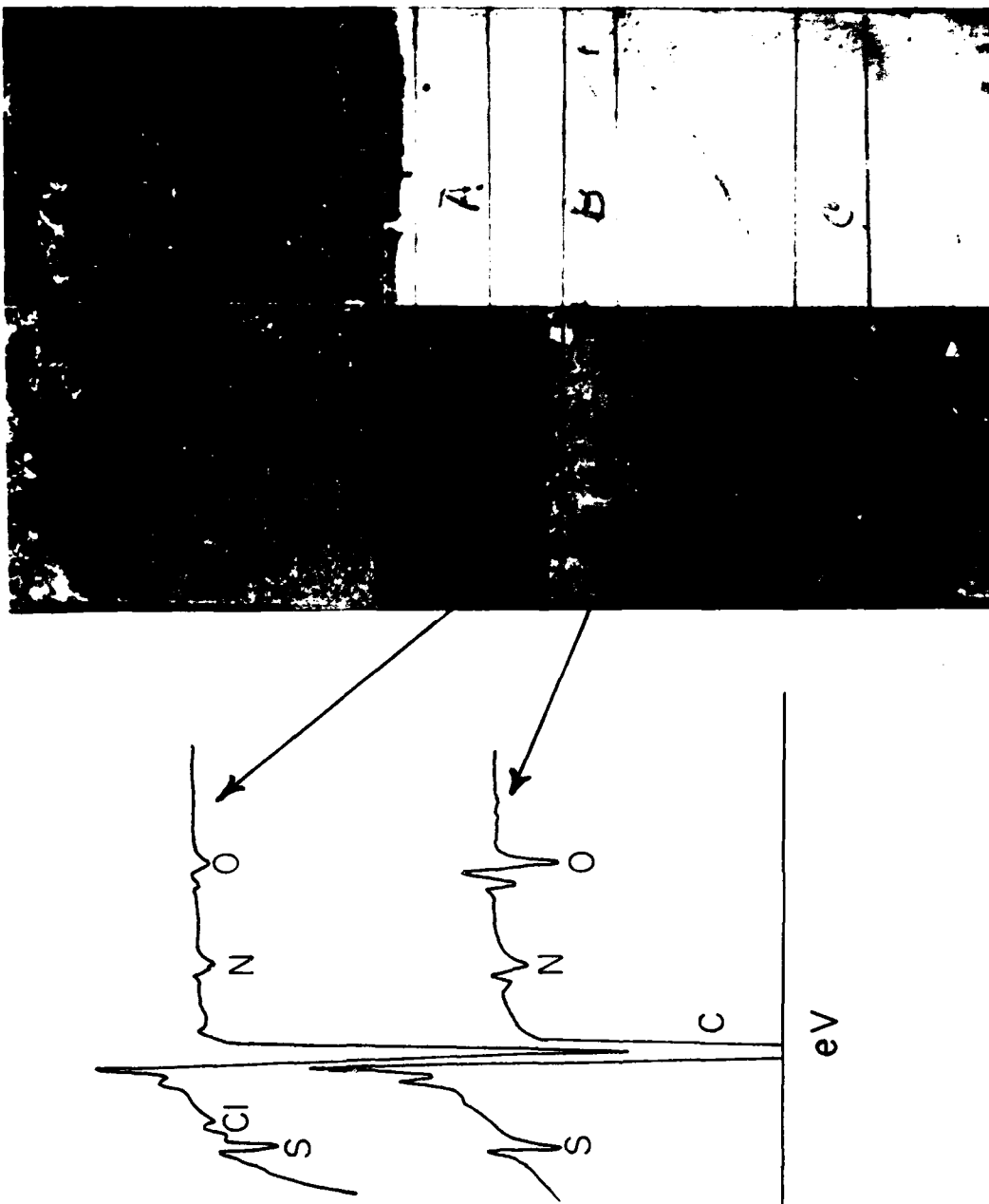


Figure 20. Adhesively Bonded Anodized 7075A1 Panels after Wedge Test with Auger Electron Spectra from the Adhesive Side of the Failed Structure at a Point which Was in Contact with a Surface Previously Exposed to Adhesive Tape (A) and a Point Not Exposed to the Tape (B)

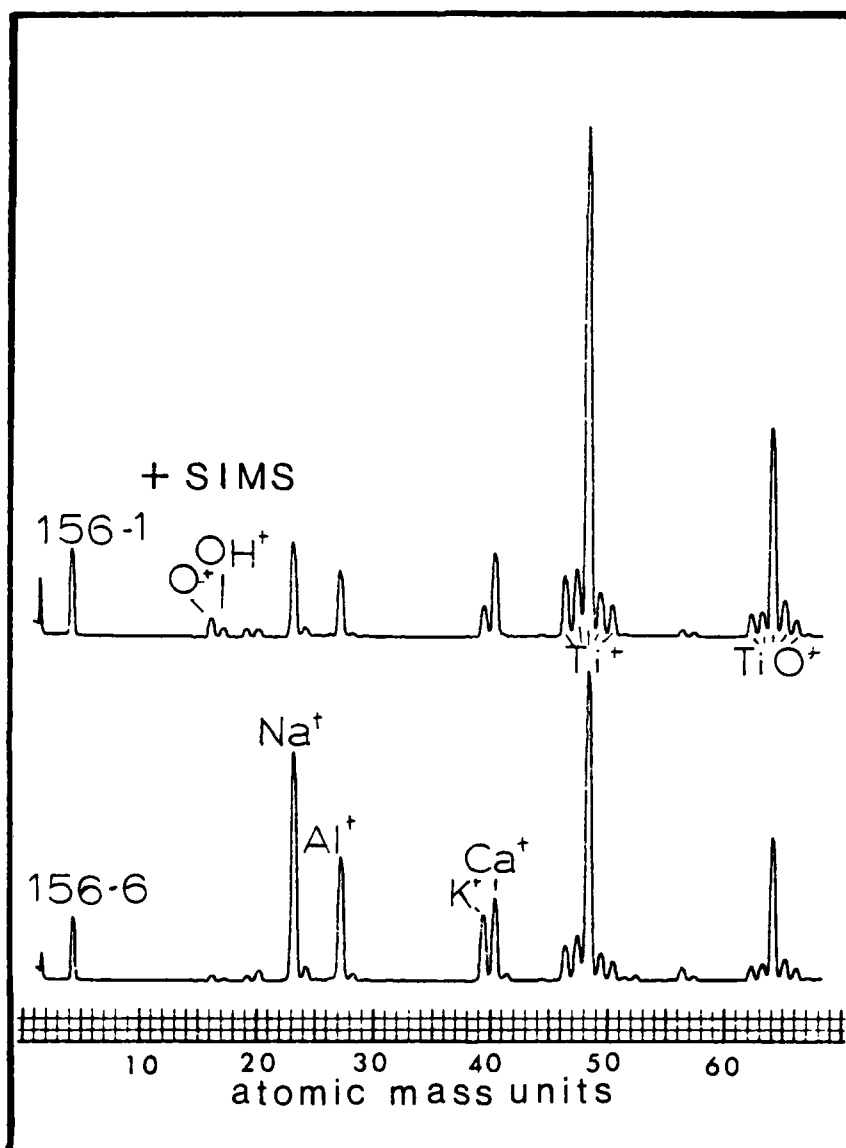


Figure 21. Positive Secondary Ion Mass Spectra from 6Al-4V-Ti at Room Temperature (156-1) and after being Treated to 350°F (156-6)

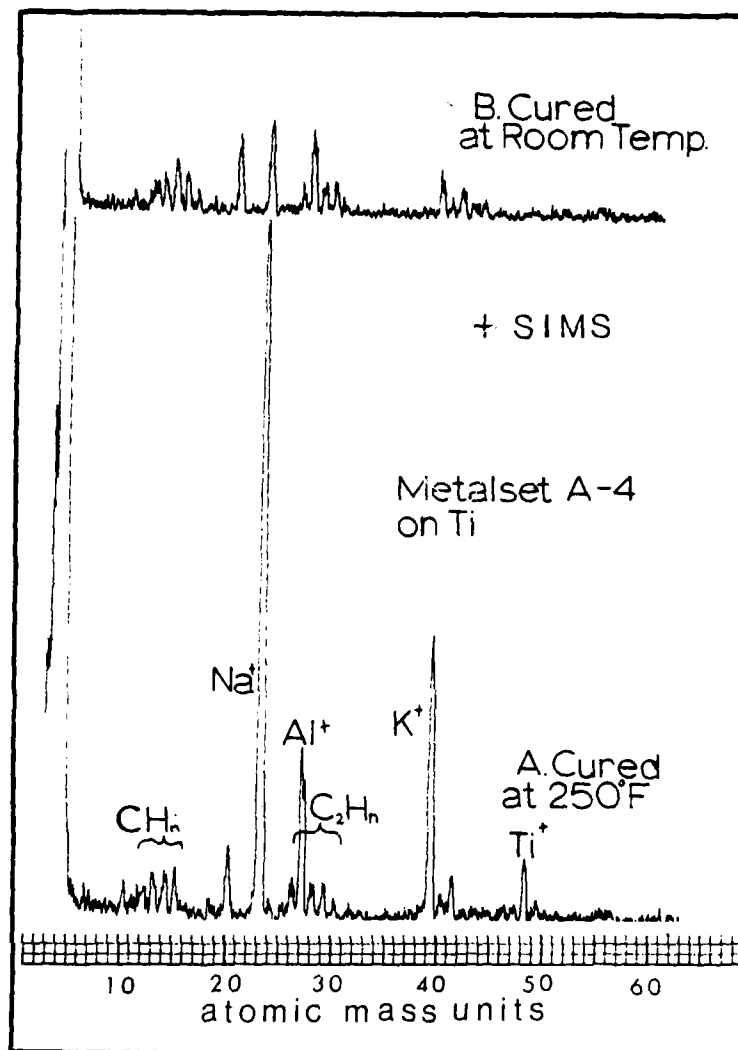


Figure 22. Positive Secondary Ion Mass Spectra from Room Temperature Cured and 250°F Cured Epoxy Adhesive

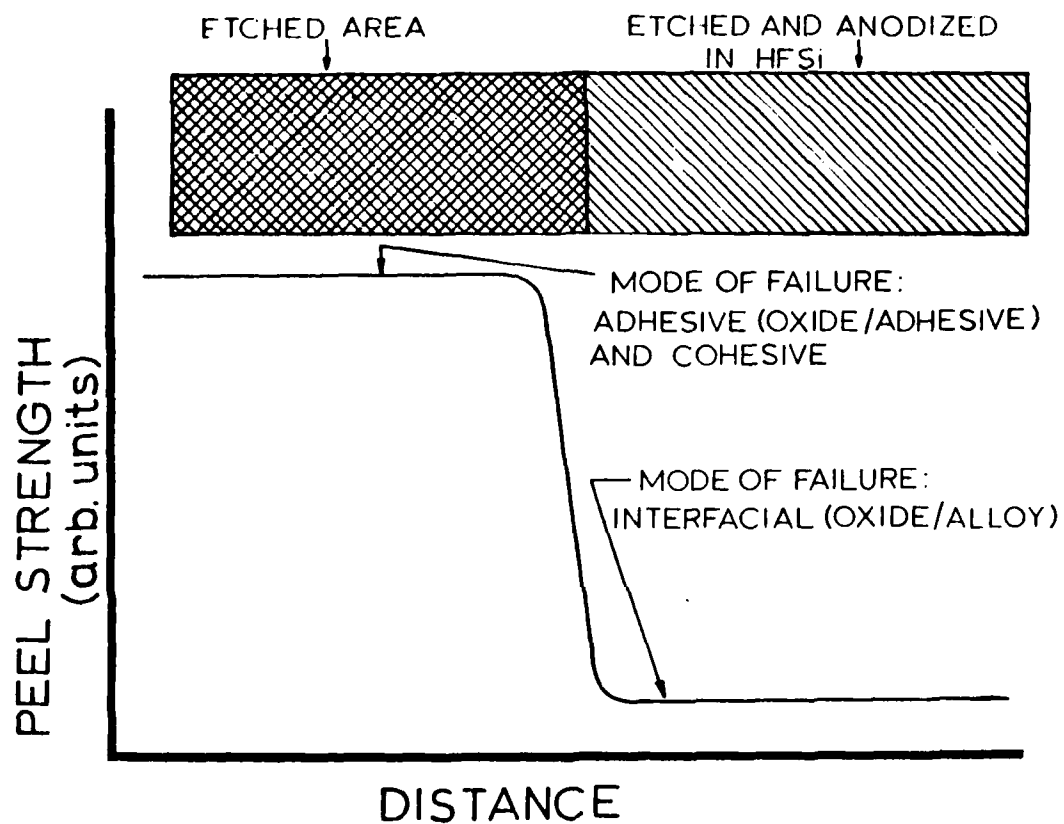


Figure 23. Results of Peel Tests in which Interfacial Oxide/Metal Failure Occurred in Anodized Specimens of Ti6Al4V

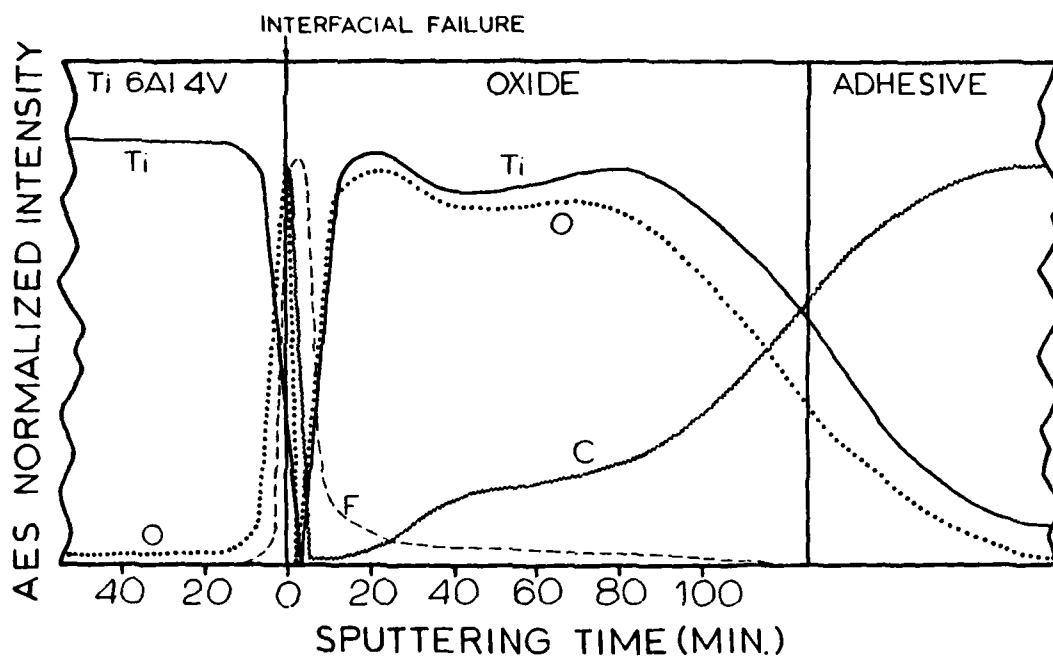


Figure 24. Elemental AES Profile of Failure Surfaces from Peel Tests Illustrated in Figure 23